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Multi-scale Cleaner Analysis of Chemical Looping Gasification Coupled Coal Pyrolysis Process

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Coal is one of combustion fuel sources that occupies an important position in the world energy resource structure. Coal pyrolysis is a very complex process involving myriad coupled reaction pathways. An in-depth mechanism investigation of coal pyrolysis will improve the efficient and cleaner coal conversion and utilisation. In this paper, a novel Coal Pyrolysis (CP) - Chemical Looping Gasification (CLG) integration strategy is proposed with the aid of multi-scale analysis to realise cleaner production of coal chemical products. First, ReaxFF molecular dynamics (MD) simulation is used to model the chemical reactions in the pyrolysis process to obtain the optimal parameters with the highest carbon conversion rate. The pyrolysis temperature should be set below 900 °C through mechanism analysis. Second, the CP-CLG system is simulated and analysed with Aspen Plus software to obtain high purity synthesis gas for synthesising cleaner coal chemical products. The mass flow of synthesis gas can reach 616.5 kg/h. Finally, one control scheme of multiple reactors is proposed to verify the stability of synthesis gas production with Aspen Dynamics software. The quality of synthesis gas is stable under different 10 % disturbances.

1. Introduction

The efficient utilisation of coal has greatly promoted environmental protection and sustainable production (Patila et al., 2018). Coal pyrolysis (CP) is the nascent decomposition pathway in the coal conversion process which accounts for up to 70 % coal transformation and has a significant impact on coal conversion operations such as gasification, liquefaction, combustion, and carbonization, etc (Larionov et al., 2019). The detailed mechanistic understanding of pyrolysis is lack due to its complex reaction environment. Quantum mechanics (QM) modelling is capable of investigating chemical bonding with high accuracy (Shen et al., 2018). The Reactive Force Field (ReaxFF) fully addresses the chemistry problems of dynamic bonds and polarisation effects in addition to the conventional bonded and nonbonded interactions in force fields (Ma et al., 2018). ReaxFF has been proven to be a smooth transition from nonbonded to bonded interactions, providing a new and promising perspective for molecular simulation of complex system with reactions. ReaxFF molecular dynamics (MD) simulation is employed to perform simulation of chemical reactions in pyrolysis of a bituminous coal model with 4,976 atoms (Mizuguchi et al., 2019). It is found that more than 900 reactions may occur at the temperature 2,000 K within the simulation period. So it is possible to explore CP mechanism for obtaining the optimal parameters with the highest carbon conversion rate through ReaxFF MD simulation. Besides, chemical looping process, as a novel coal utilization technology, utilises an indirect strategy for realising the coal conversion and CO_2 capture (Haus et al., 2018). The coal poly-generation system composed of above two processes offers the possibility to produce value-added chemicals, synthesis gas fuels, and electricity simultaneously, which can improve the coal utilisation efficiency. Kun et al. (2019) proposed a poly-generation system integrating CP and chemical looping gasification (CLG) to realise the multi-generation of value-added chemicals, synthesis gas fuels, and heat. At present, how to apply the mechanism of CP to CLG or to the purity of synthesis gas is a hot topic. This CP-CLG integration strategy aims to obtain high purity synthesis gas by means of multi-scale analysis, so it plays an important role in actual coal chemical production. Its advantages consist of cleaner production, low energy consumption, and high stability. The main steps in this novel proposal are shown in Figure 1. The structure of this paper is as follows. The coal model with the

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minimum energy is built by Materials Studio (MS) 7.0 in Section 2. ReaxFF MD simulation is used to analyse coal pyrolysis mechanism in Section 3. The CP-CLG system is simulated with Aspen Plus software in Section 4. The dynamic control of CP-CLG process is established by using Aspen Dynamics software in Section 5.

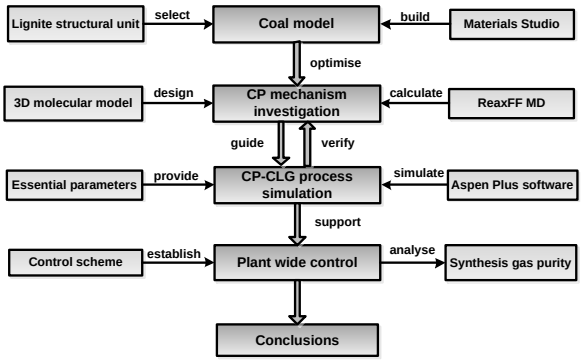

Figure 1: The flow diagram of CP-CLG integration strategy

2. Coal Model Construction

The chemical structure of coal consists of various bond types and noncovalent interactions. More than 130 molecular models have been reported over the last 70 years, indicating the complexity of coal's structure and numerous efforts in capturing its structural features (Zhang et al., 2018). To correctly reflect the aromatic properties and functional groups ratio of coal, a lignite structural unit ($C_{100}H_{80}O_{22}$) is selected as the basis of coal model as shown in Figure 2a.

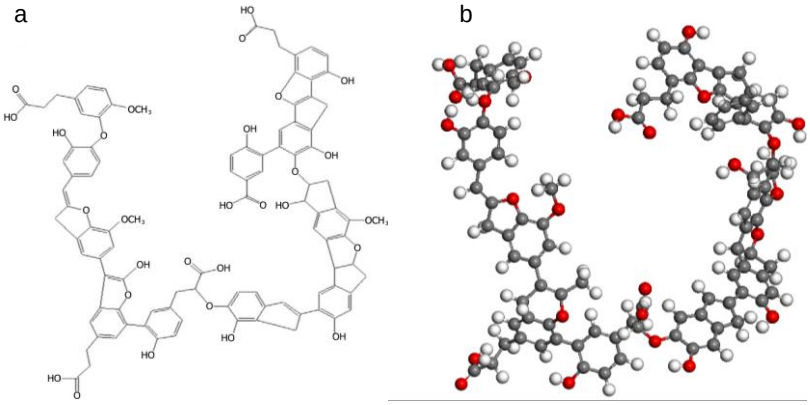

Figure 2: (a) The lignite structural unit of coal model, (b) The coal configuration with the minimum energy

The determination of coal model is the primary stage for studying the coal pyrolysis process. Above molecular model is firstly drawn in MS 7.0 and the molecular skeleton is established through sketch module. Then, the coal molecular unit structure is hydrogenated by the function of adjustable hydrogen and a reasonable initial configuration is obtained by using the clean button. Finally, forcite module is used to simulate the molecular mechanics and to optimise energy and geometry. The specific parameters are as follows: the task type is geometry optimisation, the optimisation quality is medium, and the energy optimisation method is smart. In addition, coulombian force and van der waals force are calculated by charge balance method. For the energy convergence, the convergence quality is medium, the maximum energy convergence threshold is 0.001 kcal·mol^{-1}, the maximum force convergence threshold is 0.5 kcal·mol^{-1}·Å^{-1}, and the maximum iterations is 500. Taking the minimum energy of the system as the optimisation object, the coal molecular configuration with the minimum energy of the whole potential energy surface is obtained as shown in Figure 2b.

3. CP mechanism investigation *via* ReaxFF MD

The optimised coal molecular model structure is assembled into a cubic 3D molecular model by employing the construction function of the MS amorphous cell module. The cell density is 1.2 g/cm^3, and periodic boundary

conditions are added to the cell for ensuring that the system can constantly keep the number of particles in the system. The force between atoms in the boundary is calculated by the mirror image method, so that the force is more uniform to eliminate the boundary effect. After optimising the geometry of the cell, the lowest energy geometry of coal molecular is shown in Figure 3 for ReaxFF MD simulation.

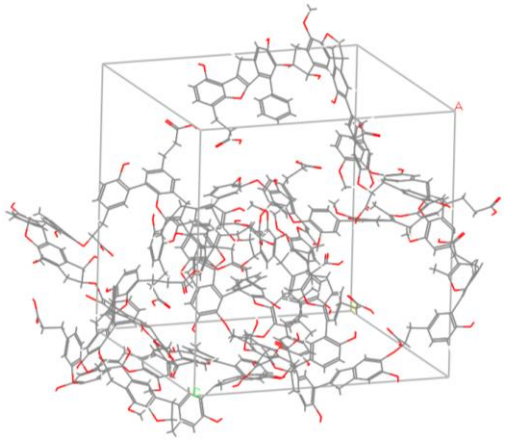

Figure 3: The lowest energy geometry of coal molecular

ReaxFF molecular dynamics is a combination of classical molecular dynamics and an empirical reactive force field, which describes the bond formation and charge transfer for complex reactive molecular systems based on the bond order concept (Torktaz et al., 2018). To carry out pyrolysis MD simulation, the coal molecular configuration obtained in MS 7.0 is exported into the Lamps software package as the initial structure of pyrolysis including the cell volume, atomic type, atomic number, and atomic coordinate information. The initial temperature of pyrolysis is 227 °C, and is increased to 1,927 °C at a rate of 20 °C/ps under the canonical ensemble system. The main operation conditions are as follows: the step size is 0.25 fs, the total simulation time is 100 ps, and the truncation coefficient of the set key is 0.3. The number of fragments with the temperature from 227 °C to 1,927 °C is shown in Figure 4. It can be seen that the coal moleculars begin to decompose into various elemental molecular gases before 800 °C such as C_1-C_4 and CO_2. Their generation is based on the breaking of weak bonds like C-O bond. From about 900 °C, a large number of H_2 moleculars emerge in the fragments due to the semi-focal polycondensation reaction. At the same time, the C-C bonds begin to break with the increasing temperature. In order to obtain high purity synthesis gas in subsequent CLG process and inhibit the production of CO_2, the pyrolysis temperature should be set below 900 °C.

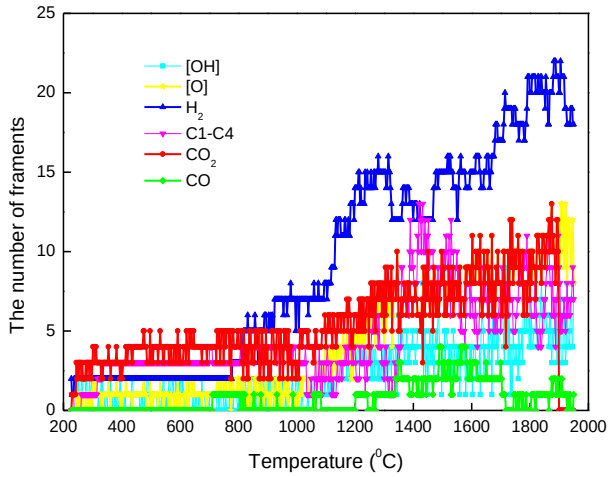

Figure 4: The variation of the number of fragments with the simulated temperature

4 CP-CLG process simulation

The simplified flow diagram of CP-CLG is shown in Figure 5, which is simulated with Aspen Plus software. In order to carry out CP-CLG process simulation, operating parameters including temperature and pressure are

obtained from a coal chemical plant. The first step for modeling the system is to take into account the special components in it. It is widely recognized that coal is composed of coal, char, and tar, which are non-conventional components in the Aspen Physical Property Database. At present, most studies have chosen the Peng Robinson-Boston Mathias (PR-BM) property method for coal pyrolysis simulation. PR-BM can be employed to accurately calculate the physical properties of the unconventional MIXED components and CISOLID components (Zhuang et al., 2018). HCOALGEN and DCOALIGT methods are used to calculate the enthalpy and density of non-conventional components in this work. In coal pyrolysis process, the drying and pyrolysis units are simulated by the RYIELD module. The temperature and pressure of drying unit are set as 130 °C and 0.1 MPa. Dry coal is obtained by removing most of water through Separator-1 (SEP1) module. After pyrolysis unit, which temperature and pressure are set as 630 °C and 1 MPa, pyrolysis gas, tar, and char are separated through SEP2 module. Char is then introduced into the RSTOIC module to yield coke. In this process, coke is decomposed and introduced into fuel reactor to react with oxygen carrier CuO for producing synthesis gas. The fuel reactor and air reactor are simulated by the RGIBBS module, allowing the calculation of reactions involving solids. The RGIBBS module runs under chemical and phase equilibrium with minimal Gibbs free energy and thermodynamic limitation. The temperature and pressure of fuel reactor are set as 950 °C and 2 MPa. The temperature and pressure of air reactor are set as 1,050 °C and 2 MPa.

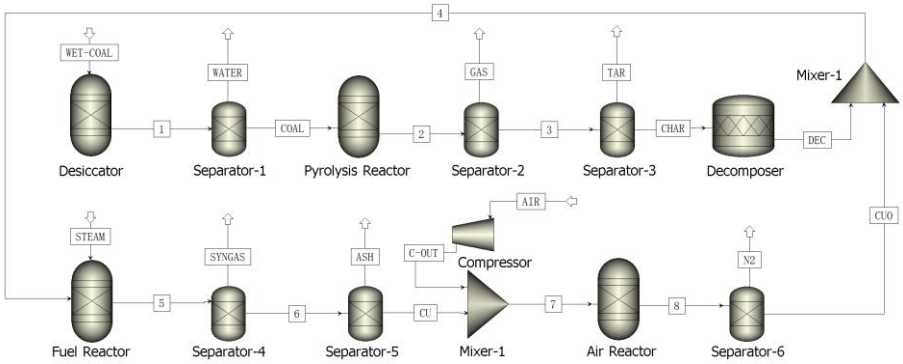

Figure 5: Simulation flowsheet of CP-CLG process in Aspen Plus software

The simulation results of major streams are listed in Table 1. The simulated values of temperature and pressure for each stream in CP-CLG process are completely consistent with the actual industrial data. It can be seen that the mass flow of H_2 and CO in SYNGAS stream are 392.8 kg/h and 223.7 kg/h, which meet the requirements of industrial production. Based on this steady-state simulation, it is necessary to analyse the effect of feed flow on synthesis gas quality in the following section.

Table 1: Simulation results of CP-CLG process

Data Item	COAL	CHAR	DEC	STEAM	Cu	CuO	SYNGAS
Actual Temperature (℃)	130	130	130	101.1	950	1,050	950
Simulated Temperature (°C)	130	130	130	101.1	950	1,050	950
Actual Pressure (MPa)	0.1	0.1	0.1	0.1	2	2	2
Simulated Pressure (MPa)	0.1	0.1	0.1	0.1	2	2	2
Vapor Fraction	0	0	0.9	1	0	0	1
Mass Flow (kg/h)	381.7	281	281	250	958.6	1,200	741.4
N_2	0	0	4.3	0	0	0	4.3
O_2	0	0	5.7	0	0	0	0
H_2O	0	0	0	250	0	0	92.1
H_2	0	0	2.4	0	0	0	**392.8**
CO	0	0	0	0	0	0	**223.7**
CO_2	0	0	0	0	0	0	0.8
C	0	0	231.1	0	0	0	0
S	0	0	6.6	0	0	0	0
ASH	0	0	31	0	0	0	0
COAL	381.7	0	0	0	0	0	0
CHAR	0	281	0	0	0	0	0
Cu	0	0	0	0	958.6	0	0
CuO	0	0	0	0	0	1,200	0

5. Plant wide control

The dynamic model of CP-CLG process is necessarily simplified by directly using coal pyrolysis products as feed stream due to the complex pyrolysis reactions and the lack of strict kinetic parameters. Table 2 lists all controller parameters including controlled variables, manipulated variables, gain and integration time (Cui et al., 2019). The dynamic control structure of CP-CLG process is shown in Figure 6, in which R01 and R02 represent fuel reactor and air reactor. Synthesis gas is obtained through FLASH module. During dynamic simulation, the impact of disturbance on the quality of synthesis gas needs to be discussed to ensure the stability of production.

Table 2: Controller parameters

Controller name	Tag number	Controlled variable	Manipulated variable	Gain K_c	Integration time T_i/min
Pressure controller	PC1	Flash pressure	V6 opening	20	12
Liquid level controller	LC1	R01 level	V5 opening	2	20
Liquid level controller	LC2	Flash level	V7 opening	2	20
Liquid level controller	LC3	R02 level	V10 opening	2	20
Flow controller	FC1	CuO feed flow	V1 opening	0.5	0.3
Flow controller	FC2	Steam feed flow	V3 opening	0.5	0.3
Temperature controller	TC1	R01 temperature	Heat input (Heater1)	2	10
Temperature controller	TC2	R02 temperature	Heat input (Heater2)	2	10

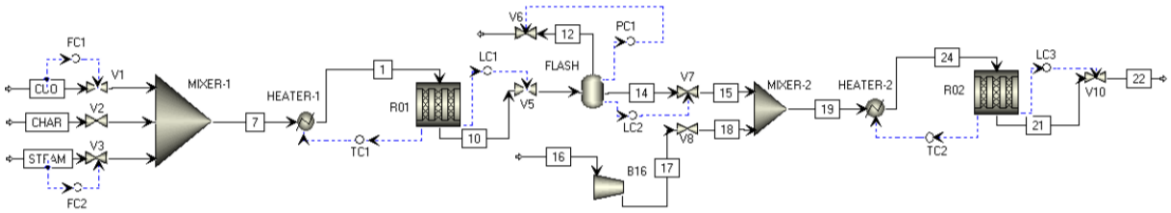

Figure 6: CP-CLG process dynamic control

The mass fraction of H_2 and CO in SYNGAS stream are analysed to ensure that the quality of synthesis gas is stable. The steam flow rate disturbance is taken as an example to test the dynamic behavior of the mass fraction of H_2 and CO in SYNGAS stream under the action of the control system. The changes of the mass fraction of H_2 and CO in SYNGAS stream after increasing steam flow rate by 10 % at 2 h are shown in Figure 7. The mass fraction of H_2 in SYNGAS stream is increased to a stable value of 0.281 and the mass fraction of CO in SYNGAS stream approaches a stable value of 0.38 gradually, which prove the validity of the control scheme depicted in Figure 6.

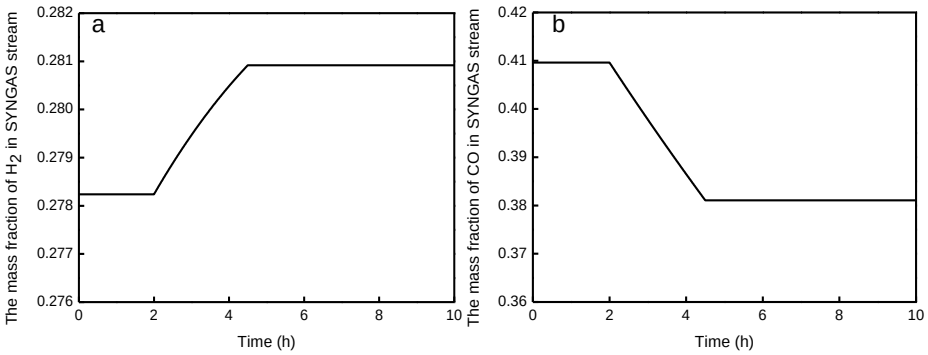

Figure 7: (a) Effect of steam flow rate disturbance at 2 h on the mass fraction of H_2 (b): Effect of steam flow rate disturbance at 2 h on the mass fraction of CO

The changes of the mass fraction of H_2 and CO in SYNGAS stream after increasing R01 reactor temperature by 10 % at 2 h are shown in Figure 8. It can be seen that the mass fraction of H_2 and CO in SYNGAS stream are increased to a stable value of 0.279 and 0.41.

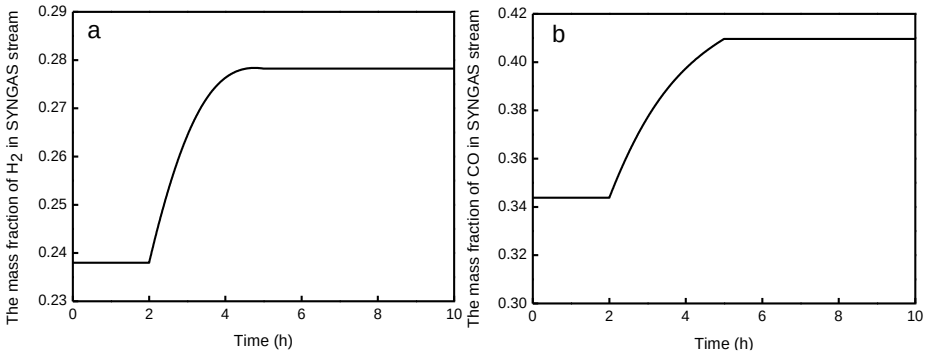

Figure 8: (a) Effect of reduction reactor temperature disturbance at 2 h on the mass fraction of H_2 (b) Effect of reduction reactor temperature disturbance at 2 h on the mass fraction of CO

6. Conclusions

This paper proposes a novel CP-CLG integration strategy with the aid of multi-scale analysis to realise clean production. The lowest energy geometry of coal molecular is established by ReaxFF MD simulation. To obtain high purity synthesis gas in CLG process and inhibit the production of CO_2, the pyrolysis temperature should be below 900 °C after mechanism investigation. The CP-CLG process is simulated with Aspen Plus software, with results showing that the mass flow of H_2 and CO in SYNGAS stream are 392.8 kg/h and 223.7 kg/h. Finally, the impact of different 10 % disturbances on the quality of synthesis gas is explored to prove the stability of production. In view of the fact that the complex reactions in coal pyrolysis have become a current topic of widespread concern in the chemical industry, the work will take into consideration more scale analysis such as chemical fluid dynamics simulation in the near future.

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References

Cui Z., Tian W., Wang X., Fan C., Guo Q., Xu, H., 2019. Safety integrity level analysis of fluid catalytic cracking fractionating system based on dynamic simulation, Journal of the Taiwan Institute of Chemical Engineers, 104, 16-26.

Haus J., Hartge E.U., Heinrich S., Werther J., 2018, Dynamic flowsheet simulation for chemical looping combustion of methane, International Journal of Greenhouse Gas Control, 72, 26-37.

Kun Z., He D., Guan J., Zhang Q., 2019, Thermodynamic analysis of chemical looping gasification coupled with lignite pyrolysis, Energy, 166, 807-818.

Larionov K.B., Mishakov I.V., Vedyagin A.A., Gubin V.E., 2019, Effect of an initiating additive of $CuSO_4$ on changes in the characteristics of brown coal oxidation and pyrolysis, Solid Fuel Chemistry, 53, 120-127.

Ma T., Hu T., Jiang D., 2018, Treatment of penicillin with supercritical water oxidation: Experimental study of combined ReaxFF molecular dynamics, Korean Journal of Chemical Engineering, 35(4), 900-908.

Mizuguchi T., Hagita K., Fujiwara S., 2019, Hydrogen bond analysis of confined water in mesoporous silica using the reactive force field, Molecular Simulation, 45(3), 1-10.

Patila M., Vaidyaa P., Kenigb E., 2018, Bench-Scale Study for CO_2 Capture Using AMP/PZ/Water Mixtures, Chemical Engineering Transactions, 69, 163-168.

Shen L., Yang W., 2018, Molecular dynamics simulations with quantum mechanics/molecular mechanics and adaptive neural networks, Journal of Chemical Theory and Computation, 14(3), 1442-1455.

Torktaz I., Najafi A., Golmohamadi R., 2018, Molecular dynamics simulation (MDS) analysis of Vibrio cholerae ToxT virulence factor complexed with docked potential inhibitors, Bioinformation, 14(3), 101-105.

Zhang S., Tang S., Zhang J., Pan, Z., 2018, Pore structure characteristics of China sapropelic coal and their development influence factors, Journal of Natural Gas Science and Engineering, 53, 370-384.

Zhuang B., Wang T., Liu J., 2018, The optical properties, physical properties and direct radiative forcing of urban columnar aerosols in the Yangtze River Delta, China, Atmospheric Chemistry and Physics, 18(2), 1419-1436.